

CLAIMS:

1. A supported chromium catalyst comprising:
chromium oxide,
a silica-containing support comprising silica selected from the group consisting of
silica having:
 - (a) a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g;
 - (b) a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g; and
 - (c) a pore volume of about 0.9 – 1.4 cm³/g and a surface area of about 390 – 590 m²/g; and,an alkyl silanol,
wherein said supported chromium catalyst is activated at 400 – 860 °C, prior to the addition of said alkyl silanol.
2. The catalyst of claim 1 further comprising titanium tetraisopropoxide.
3. The catalyst of claim 1 further comprising an organoaluminum compound.
4. The catalyst of claim 3 wherein said activated chromium catalyst is treated first with said alkyl silanol and then with said organoaluminum compound.
5. The catalyst of claim 3 wherein said silica has a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g and said organoaluminum compound is an alkyl aluminum alkoxide compound.
6. The catalyst of claim 3 wherein said silica has a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g, and said organoaluminum compound is an alkyl aluminum alkoxide compound.
7. The catalyst of claim 3 wherein said organoaluminum compound is added in-situ.

8. The catalyst of claim 3 further comprising at least a second chromium-based compound.
9. The catalyst of claim 8 wherein said second chromium-based compound is a chromium oxide on silica or an organoaluminum-reduced chromium oxide on silica.
10. The catalyst of claim 3 wherein said alkyl silanol or said organoaluminum compound or both said alkyl silanol and said organoaluminum compound are added in-situ.
11. The catalyst of claim 10 wherein said alkyl silanol and said organoaluminum compound are pre-mixed prior to said in-situ addition.
12. The catalyst of claim 3 wherein said organoaluminum compound is an alkyl aluminum alkoxide compound.
13. The catalyst of claim 12 wherein said alkyl aluminum alkoxide compound is diethyl aluminum ethoxide.
14. The catalyst of claim 12 formed by the in situ addition of said alkyl aluminum alkoxide compound.
15. The catalyst of claim 14 wherein said alkyl aluminum alkoxide compound is diethyl aluminum ethoxide.
16. The catalyst of claim 3 wherein said organoaluminum compound is an alkyl aluminum compound.
17. The catalyst of claim 16 wherein said alkyl aluminum compound is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.

18. The catalyst of claim 17 formed by the in situ addition of said alkyl aluminum compound.
19. The catalyst of claim 17 wherein said alkyl aluminum compound is tri-isobutyl aluminum.
20. The catalyst of claim 1 wherein said supported chromium catalyst is activated at 600 – 860 °C.
21. The catalyst of claim 1 wherein said alkyl silanol is triphenyl silanol
22. A supported chromium catalyst comprising:
chromium oxide,
a silica-containing support comprising silica selected from the group consisting of silica having:
 - (a) a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g;
 - (b) a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g; and
 - (c) a pore volume of about 0.9 – 1.4 cm³/g and a surface area of about 390 – 590 m²/g; and,an organoaluminum compound,
wherein said supported chromium catalyst is activated at 400 – 860 °C.
23. The catalyst of claim 22 wherein said organoaluminum compound is diethyl aluminum triethylsiloxide.
24. The catalyst of claim 22 further comprising titanium tetraisopropoxide.
25. A supported chromium catalyst comprising:
chromium oxide,
a silica-containing support comprising silica selected from the group consisting of silica having:

- (a) a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g;
- (b) a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g; and
- (c) a pore volume of about 0.9 – 1.4 cm³/g and a surface area of about 390 – 590 m²/g;

wherein said supported chromium catalyst is activated at 400 – 860 °C; and, a second chromium-based compound comprising silylchromate on silica treated with an organoaluminum compound.

26. The catalyst of claim 25 wherein said chromium oxide catalyst component is treated with an organoaluminum compound after activation.
27. The catalyst of claim 25 further comprising titanium tetraisopropoxide.
28. A process for producing an ethylene polymer comprising the steps of:
contacting ethylene under polymerization conditions with a catalyst system, said catalyst system comprising chromium oxide, an alkyl silanol compound, and a silica-containing support comprising silica selected from the group consisting of silica having:
 - (a) a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g;
 - (b) a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g; and
 - (c) a pore volume of about 0.9 – 1.4 cm³/g and a surface area of about 390 – 590 m²/g;and,
controlling one or more of catalyst activity, polymer Mz/Mw, polymer Mw/Mn, and polymer density of the resulting ethylene polymer by varying the level of addition of said alkyl silanol.
29. The process of claim 28 wherein said polymer Mw/Mn is controlled to greater than about 15 and said polymer Mz/Mw is controlled to greater than about 5.

30. The process of claim 28 wherein said catalyst system further comprises an organoaluminum compound.
31. The process of claim 30 wherein said catalyst system further comprises at least a second chromium-based catalyst.
32. The process of claim 31 wherein said second chromium-based compound is a chromium oxide on silica or an organoaluminum-reduced chromium oxide on silica.
33. The process of claim 30 wherein said organoaluminum compound is an alkyl aluminum alkoxide.
34. The process of claim 33 wherein said alkyl aluminum alkoxide comprises diethylaluminum ethoxide.
35. The process of claim 30 wherein said organoaluminum compound is an alkyl aluminum compound.
36. The process of claim 35 wherein said alkyl aluminum compound is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
37. The process of claim 28 wherein said catalyst system further comprises titanium tetraisopropoxide.
38. A process for producing an ethylene polymer comprising the steps of:
contacting ethylene under polymerization conditions with a catalyst system, said catalyst system comprising chromium oxide,
a silica-containing support comprising silica selected from the group consisting of
silica having:

(a) a pore volume of about 1.1 – 1.8 cm³/g and a surface area of about 245 – 375 m²/g;

(b) a pore volume of about 2.4 – 3.7 cm³/g and a surface area of about 410 – 620 m²/g, and

(c) a pore volume of about 0.9 – 1.4 cm³/g and a surface area of about 390 – 590 m²/g;

wherein said supported chromium catalyst is activated at 400 – 860 °C; and,
a second chromium-based compound comprising silylchromate on silica treated
with an organoaluminum compound;

and,

controlling one or more of polymer molecular weight, polymer Mz/Mw, polymer
Mw/Mn, and distribution of comonomer incorporation by varying the
relative amount of each of said chromium oxide and said second
chromium-based compound.

39. The process of claim 38 wherein said chromium oxide catalyst component is treated with an organoaluminum compound after activation.
40. The process of claim 38 wherein said catalyst system further comprises titanium tetraisopropoxide.
41. An ethylene polymer having a density of 0.918 – 0.970 g/cm³ and a flow index (I₂₁) of 1 – 500 and produced by the process of claim 28.
42. An ethylene polymer having a density of 0.918 – 0.970 g/cm³ and a flow index (I₂₁) of 1 – 500 and produced by the process of claim 30.
43. An ethylene polymer having a density of 0.918 – 0.970 g/cm³ and a flow index (I₂₁) of 1 – 500 and produced by the process of claim 31.
44. An ethylene polymer having a density of 0.918 – 0.970 g/cm³ and a flow index (I₂₁) of 1 – 500 and produced by the process of claim 32.

45. An ethylene polymer having a density of 0.918 – 0.970 g/cm³ and a flow index (I₂₁) of 1 – 500 and produced by the process of claim 38.